



# Synthesis of $\text{Ce}_a\text{MnO}_x$ hollow microsphere with hierarchical structure and its excellent catalytic performance for toluene combustion

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## ABSTRACT

A series of  $\text{Ce}_a\text{MnO}_x$  hollow microsphere like arbutus with hierarchical structure are prepared by redox co-precipitation method and applied for catalytic toluene combustion. The  $\text{Ce}_{0.03}\text{MnO}_x$  shows a better catalytic performance for toluene combustion with high stability, water resistance, even under the condition of 5vol.%  $\text{H}_2\text{O}$ . The results of XRF, XRD, Raman,  $\text{N}_2$  adsorption-desorption, SEM, TEM prove that the doping of Ce can affect the structure of  $\text{Ce}_a\text{MnO}_x$  such as much smaller particle size and higher specific surface area. The characterizations of  $\text{H}_2$ -TPR,  $\text{O}_2$ -TPD, XPS certify the strong interaction between Ce and Mn oxides that leads to more surface adsorbed oxygen and  $\text{Mn}^{4+}$  species due to oxidation reduction cycle of  $\text{Mn}^{3+} + \text{Ce}^{4+} \leftrightarrow \text{Mn}^{4+} + \text{Ce}^{3+}$  after Ce addition. Meanwhile, the Toluene-TPD in different conditions confirms the introduction of water promoted the catalytic oxidation of toluene. *In situ* DRIFTS is used to investigate the reaction process of toluene oxidation. And the results reveal that the  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst has much stronger ability to adsorb and activate toluene compared with  $\text{MnO}_x$  catalyst, especially under with  $\text{H}_2\text{O}$ . That may be the main reason that the  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst exhibits the special catalytic activity for toluene combustion.

## 1. Introduction

Volatile organic compounds (VOCs) are a group of chemicals such as hydrocarbon, esters, aldehydes, etc., which are released from industrial process, incomplete combustion, paint materials and other activities related to human [1,2]. VOCs are regarded as not only one of the most contributors to air pollution, but also the main hazardous substances with great damage effect on public health [2,3]. Accordingly, it is impending to reduce effectively VOCs emission. Nowadays, several abatement technologies such as photocatalysis [4–6], thermal oxidation, wet scrubbing [7], catalytic oxidation and so on have been used to control the release of VOCs.

Among all the applied control technologies, catalytic oxidation is considered one of the most hopeful environmental technologies for VOC treatment because of its higher treatment efficiency, lower reaction temperature and less energy consumption [8]. In the past few years, a large number of catalysts about VOCs catalytic oxidation have been reported by the researchers. Generally, catalysts for VOCs combustion are classified into two categories including noble metals (Pt, Au, Pd, Ag) [9–14] and transition metal oxide catalysts. However, the

usage of the noble metal as catalyst is limited due to high cost, low thermal stability and easy deactivation. Compared with noble metals, transition metal oxide catalysts have attracted extensive attention because of its high catalytic activity, lower costs and higher resistance to poisons.

In these transition metal oxide catalysts, Mn [15–19], Ce [20–22], Cu [23,24], Nb [25] and Co [26–31]-base oxides are considered as the most efficient catalysts for VOCs combustion based on their strong oxidation properties. Manganese oxides ( $\text{MnO}_x$ ) are considered as the much better catalysts for catalytic hydrocarbons oxidation at low temperature because of their strong oxidizability derived from the structural property of Mn [32,33]. So in the past ten years,  $\text{MnO}_x$  with different morphology and structures has been extensively studied in catalytic combustion of hydrocarbons. For example, Dai et al. [15] synthesized a series of manganese oxides including rod-like, wire-like, tubular  $\alpha\text{-MnO}_2$ , and flower-like spherical  $\text{Mn}_2\text{O}_3$  by the hydrothermal method and the  $\text{CCl}_4$  solution method, which were used remove toluene and the rod-like  $\alpha\text{-MnO}_2$  showed the better catalytic performance due to its high adsorbed oxygen concentration. Li's group [16] prepared 3DOM  $\gamma\text{-MnO}_2$ -like *via* hard template, which was also responsible for

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the excellent catalytic performance because of the mesoporous structure and  $O_{\text{lat}}$  mobility. Tang et al. [17] synthesized high surface area mesoporous manganese oxide by a novel template-free oxalate route, and the catalyst exhibited high stability. In addition, lots of metal oxides materials with hierarchical structure were prepared and used to electrochemistry that displayed specific electrochemical performance compared with traditional oxides [34,35]. In general, manganese oxide with special structure exhibits the much better performance than the traditional  $MnO_x$ .

Furthermore,  $CeO_2$ , as a rare earth oxide, has been extensively investigated in heterogeneous catalysis based on its excellent storage/release capacity of oxygen. Wang et al. [36] synthesized  $Ce_xMn_{1-x}$  composite oxides via hydrothermal process which exhibited good activity because of crystal defects and synergistic effect between Mn and Ce. Wang et al. prepared Ce-Mn oxides by sol-gel method and exhibited high ability and activity to remove chlorobenzene [37]. Moreover, Chen et al. reported that CeMn composite oxides were synthesized by using hydrolysis driving redox co-precipitation method which showed the excellent performance of catalytic oxidation of VOCs (toluene, benzene, o-xylene and chlorobenzene) [38].

Therefore, we would consider whether the synergistic effect between Ce and Mn oxides could be effective for enhancing the catalytic oxidation ability. In order to improve the synergistic effect,  $MnO_x$  modified by Ce with hierarchical structure is considered for design and synthesis based on above description.

In this work, a series of  $Ce_aMnO_x$  materials with hierarchical structure are prepared by redox co-precipitation method and applied for catalytic toluene combustion. The relation between catalyst structure and catalytic activity are investigated by various characterizations. The purpose of this paper is to understand the effects of Ce on the structure and the catalytic performance of  $Ce_aMnO_x$ .

## 2. Experimental

### 2.1. Catalysts preparation

$Ce_aMnO_x$  hollow microspheres like arbutus with hierarchical structure were prepared by redox co-precipitation method. Briefly, 2.500 g  $KMnO_4$  and 1.060 g  $MnSO_4$  were dissolved by distilled water, and added an appropriate amount of  $Ce(NO_3)_3 \cdot 6H_2O$  (0.191–0.478 g) according to the molar ratio of Ce to Mn (0.02, 0.03, 0.04 and 0.05). Concentrated hydrochloric acid was added to the mixture to change the pH. Next, 2 mL polyethylene glycol 400 (PEG 400) was added into the solution and then stirring for two hours. After that, the mixture was filtrated and the solid sample was dried in the oven at 100 °C overnight. Finally, the product was calcined in muffle furnace at 500 °C for 3 h at a ramp of 5 °C min<sup>-1</sup> to obtain the  $Ce_aMnO_x$  ( $a = 0.02, 0.03, 0.04$  and 0.05) catalysts. Additionally, the sample  $MnO_x$  was also prepared according to above process without adding  $Ce(NO_3)_3 \cdot 6H_2O$ .

### 2.2. Catalyst characterization

X-ray diffraction (XRD) pattern was obtained by a Bruker D8 Advance equipped with a  $Cu K\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ). Raman spectrum was measured using a Jobin Yvon HR 800 micro-Raman spectrometer at 458 nm. The Brunauer-Emmett-Teller (BET) surface area ( $S_{\text{BET}}$ ) was conducted on the Micromeritics Tristar II 3020 instrument at liquid  $N_2$  temperature (−196 °C). X-ray fluorescence (XRF) spectrometer was used to detect the chemical composition by Bruker S4 Explorer instrument. Surface atomic concentration and chemical states of the elements were measured by X-ray photoelectron spectrometer by a Kratos-AXIS ULTRA DLD with an Al  $K\alpha$  radiation source. Scanning electron microscope (SEM) images were obtained using a Hitachi S-4800 microscope at 20 kV and Transition electron microscope (TEM) images were attained by JEOL JEM-2010 F at an accelerating voltage of 200 kV.

Temperature programmed reduction with  $H_2$  ( $H_2$ -TPR) was performed by the TP-5080 AutoChem adsorption analyzer (Xianquan) equipped with a thermal conductivity detector. Firstly, the catalyst (0.0200 g) was pretreated at the steam of  $O_2$  with the flow rate of 30 mL min<sup>-1</sup> for 30 min at 300 °C and cooled down to 30 °C at the same airstream condition. Then the treated catalyst was heated from 30 °C to 800 °C with a rate of 10 °C min<sup>-1</sup> in a 5%  $H_2/N_2$  flow (30 mL min<sup>-1</sup>). Temperature programmed desorption of  $O_2$  ( $O_2$ -TPD) was conducted on the TP-5080 AutoChem adsorption analyzer. 0.100 g sample was pretreated under  $O_2$  atmosphere (30 mL min<sup>-1</sup>) at 300 °C for 30 min and cooled down to 30 °C at the same airstream condition. Then the treated catalyst was heated from 30 °C to 800 °C with a rate of 10 °C min<sup>-1</sup> in a He flow (30 mL min<sup>-1</sup>). Oxygen temperature programmed surface reaction ( $O_2$ -TPSR) test was carried on the same instrument with  $H_2$ -TPR. At first, the catalyst (0.050 g) was pre-treated in He at 300 °C for 30 min and cooled it to 50 °C. Then the sample adsorbed toluene for 15 min and was purged by He for 20 min. Finally, the TPSR run was tested under a flow of 30 mL min<sup>-1</sup> 3 vol%  $O_2/He$  ramping at 10 °C min<sup>-1</sup> to 500 °C and the signal was detected by a mass spectrometer (MS) at mass-to-charge ( $m/z$ ) ratios of 18 ( $H_2O$ ), 28 (CO), 44 ( $CO_2$ ), 92 (toluene) and 106 (benzaldehyde). Toluene-TPD was detected by the same apparatus with different adsorption conditions (Toluene, Toluene +  $O_2$ , Toluene +  $O_2$  +  $H_2O$ ). After adsorption, He was purged for 20 min. Then the temperature was raised to 500 °C under He and MS signals were detected.

The *in situ* DRIFTS study was carried out through FTIR spectrometer (Nicilet 6700) equipped with a DRIFTS cell (Harrick) and a highly sensitive MCT detector cooled by liquid  $N_2$  in the range of 650–4000 cm<sup>-1</sup> with 64 scans. Firstly, the sample was loaded on the IR cell and heated to 300 °C for 30 min in the  $N_2$  atmosphere in order to remove the adsorbed gas, and then the temperature decreased to 220 °C to collect the background. Then, the toluene with  $N_2$  as carrier was introduced to the cell under a flow rate of 100 mL min<sup>-1</sup> at 220 °C for 100 min, and the DRIFTS were recorded. After then,  $N_2$  was inlet about 1 h to remove physical adsorbed toluene. Finally, 20%  $O_2/N_2$  was inlet to the cell to record the spectrum.

### 2.3. Activity tests of catalytic

The catalytic activities were performed in a tubular fixed bed reactor system connected an online gas chromatography (GC) equipped with a flame ionization detector (FID) and a KB-1 column (30 m × 0.25 mm × 0.25 μm). The gas mixture contained 1000 ppm toluene, 5 vol.% of water vapor (when used), 18 vol.%  $O_2$  and  $N_2$  as balance gas. The total reactive gas was intermixed in tubular fixed bed and the flow velocity was 100 mL min<sup>-1</sup>, giving weight hourly space velocity (WHSV) of 20,000 mL h<sup>-1</sup> g<sup>-1</sup> with 0.300 g catalyst of 40–60 meshes. The activities were also measured under different WHSV of 40,000 and 80,000 mL g<sup>-1</sup> h<sup>-1</sup>. Water resistance performance was tested under 5 vol.%, 10 vol.% and 20 vol.%  $H_2O$  passing the feed stream through a water saturator at 240 °C.

The toluene conversion ( $X_{\text{toluene}}$ ) was calculated at different temperature as below Eq. (1).

$$X_{\text{toluene}} = (c(\text{toluene})_{\text{outlet}} / c(\text{toluene})_{\text{inlet}}) \times 100\% \quad (1)$$

Where,  $c(\text{toluene})_{\text{outlet}}$  and  $c(\text{toluene})_{\text{inlet}}$  represent the outlet and inlet concentration of toluene, respectively.

TON values were calculated at 200 and 220 °C as below Eq. (2).

$$TON = \frac{\left(\frac{P_v}{RT}\right)\alpha}{m_{\text{cat}}\beta_{Mn}/M_{Mn}} t \quad (2)$$

Where  $P$  is saturated vapor pressure of toluene at 5 °C ( $1.227 \times 10^3 \text{ Pa}$ );  $v$  is toluene flow rate (8.15 mL min<sup>-1</sup>);  $R$  is proportional constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>);  $\alpha$  is toluene conversion at different test temperature (200 and 220 °C);  $T$  is the temperature (278 K);  $m_{\text{cat}}$  is catalyst

**Table 1**  
Pore structure parameter and XRF results of the  $\text{Ce}_a\text{MnO}_x$  samples.

Sample	Crystal size (nm) <sup>a</sup>	Element contents (at.%) <sup>b</sup>			BET surface area ( $\text{m}^2 \text{g}^{-1}$ )	BJH pore size (nm)	Pore volume ( $\text{m}^3 \text{g}^{-1}$ )
		Mn	Ce	Ce/Mn <sup>c</sup>			
$\text{MnO}_x$	21.4	100	–	–	27.8	25.8	0.18
$\text{Ce}_{0.02}\text{MnO}_x$	17.9	98.66	1.34	0.014	47.5	21.7	0.26
$\text{Ce}_{0.03}\text{MnO}_x$	16.6	98.24	1.86	0.019	51.2	18.5	0.24
$\text{Ce}_{0.04}\text{MnO}_x$	13.9	97.17	2.83	0.029	71.3	16.7	0.3
$\text{Ce}_{0.05}\text{MnO}_x$	13.5	97.07	2.93	0.030	79.5	13.9	0.28

<sup>a</sup> Calculated by the XRD data.

<sup>b</sup> Data of element content is determined by the XRF analysis.

<sup>c</sup> Atomic ratio of Ce to Mn in bulk  $\text{Ce}_a\text{MnO}_x$ .

mass;  $\beta_{\text{Mn}}$  is the Mn loading content of XPS data;  $M_{\text{Mn}}$  is relative atomic mass ( $54.938 \text{ g mol}^{-1}$ );  $t$  is reaction time which is 1 min.

### 3. Results and discussion

The element composition of samples in bulk is confirmed by XRF analysis and shown in Table 1. It is easy to see that the molar ratio of Ce to Mn (Ce/Mn) in  $\text{Ce}_a\text{MnO}_x$  is 0.014, 0.019, 0.029 and 0.030 for  $\text{Ce}_{0.02}\text{MnO}_x$ ,  $\text{Ce}_{0.03}\text{MnO}_x$ ,  $\text{Ce}_{0.04}\text{MnO}_x$  and  $\text{Ce}_{0.05}\text{MnO}_x$ , respectively, and it increases gradually with doping more amount of Ce. However, it is noteworthy that the measured Ce/Mn ratio is lower than the corresponding theoretical value (0.02, 0.03, 0.04 and 0.05) in  $\text{Ce}_a\text{MnO}_x$ . Moreover, the Ce/Mn ratio only increases slightly when the theoretical Ce/Mn ratio increases from 0.04 to 0.05 in the synthesis process. In addition, the theoretical Ce/Mn value in the  $\text{Ce}_a\text{MnO}_x$  is used in this paper in order to describe conveniently.

#### 3.1. XRD and Raman results

The crystal phase of these  $\text{Ce}_a\text{MnO}_x$  samples was tested by XRD, and the results are shown in Fig. 1(A). For all samples, the diffraction peaks at  $23.1^\circ$ ,  $33.0^\circ$ ,  $38.2^\circ$  and  $55.2^\circ$  correspond to (211), (222), (400) and (440) planes of bixbyite  $\text{Mn}_2\text{O}_3$  (PDF 41–1442) [39,40], respectively. As shown in Fig. 1(A), no new characteristic peaks assigned the cerium oxide appeared for  $\text{Ce}_a\text{MnO}_x$ , which may be due to too little Ce content that is beyond the detection limit, Ce element is introduced the lattice of  $\text{MnO}_x$ , or the Ce oxide highly dispersed in  $\text{MnO}_x$ . However, the radius of  $\text{Ce}^{3+}$  (0.134 nm) and  $\text{Ce}^{4+}$  (0.114 nm) are much larger than that of  $\text{Mn}^{3+}$  (0.064 nm) and  $\text{Mn}^{4+}$  (0.060 nm), so Ce can not incorporate into the  $\text{MnO}_x$  lattice. Moreover, the peak intensity gets weaker and weaker with the increase in the Ce content. The results indicate the existence of Ce could lower the crystallinity of  $\text{Ce}_a\text{MnO}_x$  [41]. The crystal size was calculated by using Scherrer equation with

the peak width at half height of diffraction peaks at  $23.1^\circ$ ,  $33.0^\circ$  and  $38.2^\circ$ . As displayed in the Table 1, the crystal size is 21.4, 17.9, 16.6, 13.9 and 13.5 nm for  $\text{MnO}_x$ ,  $\text{Ce}_{0.02}\text{MnO}_x$ ,  $\text{Ce}_{0.03}\text{MnO}_x$ ,  $\text{Ce}_{0.04}\text{MnO}_x$  and  $\text{Ce}_{0.05}\text{MnO}_x$ , respectively, suggesting that it decreases gradually with the increase of the Ce content. Interesting, it is found that there is a good linear relation between crystal size and the measured Ce content in  $\text{Ce}_a\text{MnO}_x$  (Fig. 1(B)). To sum up, there is a strong interaction between Ce and Mn oxides and Ce oxide is highly dispersed on the surface of  $\text{Ce}_a\text{MnO}_x$ .

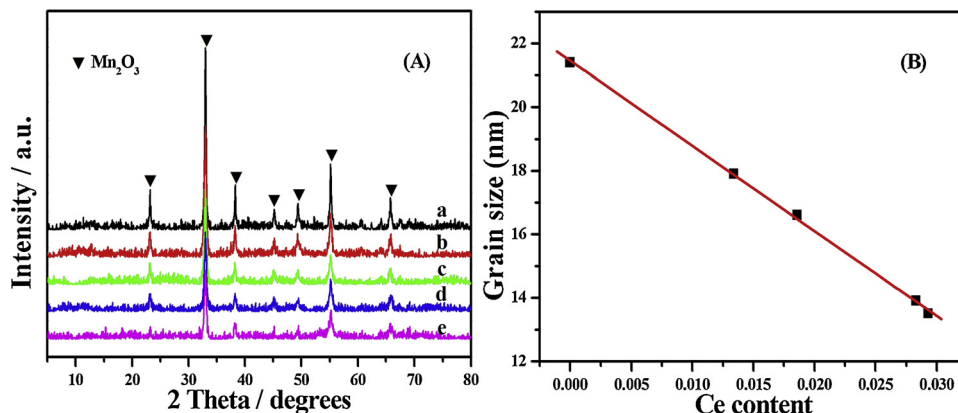
To gain more insight on the structure of catalyst, the samples are characterized by Raman spectroscopy. As presented in Fig. S1, the bands at  $365$  and  $652 \text{ cm}^{-1}$  for  $\text{MnO}_x$  belong to the out-of-plane bending modes and symmetric stretching of  $\text{Mn}_2\text{O}_3$  groups, respectively [39,42]. It must be also mentioned that the peaks at  $365$  and  $652 \text{ cm}^{-1}$  for  $\text{Ce}_a\text{MnO}_x$  become weaker than those of  $\text{MnO}_x$ , suggesting that the strong interaction between Mn and Ce, which is consistent with the results of XRD.

#### 3.2. $\text{N}_2$ adsorption-desorption measurements

Fig. 2 displays the  $\text{N}_2$  adsorption-desorption isotherms (Fig. 2(A)) and the pore size distribution (Fig. 2(B)) of the  $\text{Ce}_a\text{MnO}_x$  samples. All samples show the type IV isotherms and possess a distinct H3 type hysteresis loop at relative pressure range at 0.87–1.0, 0.80–1.0, 0.76–1.0, 0.69–1.0 and 0.65–1.0 for  $\text{MnO}_x$ ,  $\text{Ce}_{0.02}\text{MnO}_x$ ,  $\text{Ce}_{0.03}\text{MnO}_x$ ,  $\text{Ce}_{0.04}\text{MnO}_x$  and  $\text{Ce}_{0.05}\text{MnO}_x$ , respectively, indicating that they have similar mesoporous structure [43,44]. Furthermore, the wider range of pore structure is acquired with the leading of Ce, suggesting the pore structure is not neat. Additionally, their average pore sizes are 25.8, 21.7, 18.5, 16.7 and 13.9 nm, and the corresponding specific BET surface area is 27.8, 47.5, 51.2, 71.3 and  $79.5 \text{ m}^2 \text{g}^{-1}$ . The results demonstrate the pore size reduces and the BET surface area increases with the Ce addition. Meanwhile, the pore size and the specific surface area have linear relation with bulk Ce content, respectively (Fig. S2). Hence, it can be conclude that the addition of Ce has obvious influence on the structure of the  $\text{Ce}_a\text{MnO}_x$  samples, also confirming the strong interaction between Mn and Ce.

#### 3.3. SEM images

SEM images of the samples are shown in Fig. 3. The morphology of  $\text{MnO}_x$  presents microsphere like arbutus (Fig. 3(a) and (b)) possessing lots of doming on the surface of  $\text{MnO}_x$  and the size of about 800 nm. Both  $\text{Ce}_{0.02}\text{MnO}_x$  and  $\text{Ce}_{0.03}\text{MnO}_x$  show the arbutus-like microspheres and the size is 500 and 430 nm, respectively. Furthermore, both  $\text{Ce}_{0.04}\text{MnO}_x$  and  $\text{Ce}_{0.05}\text{MnO}_x$  are hollow shell structure with open mouth and the size reduces to 370 and 350 nm, respectively. This phenomenon may be because the strong interaction between Mn and



**Fig. 1.** (A) XRD patterns of  $\text{MnO}_x$  (a),  $\text{Ce}_{0.02}\text{MnO}_x$  (b),  $\text{Ce}_{0.03}\text{MnO}_x$  (c),  $\text{Ce}_{0.04}\text{MnO}_x$  (d) and  $\text{Ce}_{0.05}\text{MnO}_x$  (e) and (B) crystal size with different Ce content.

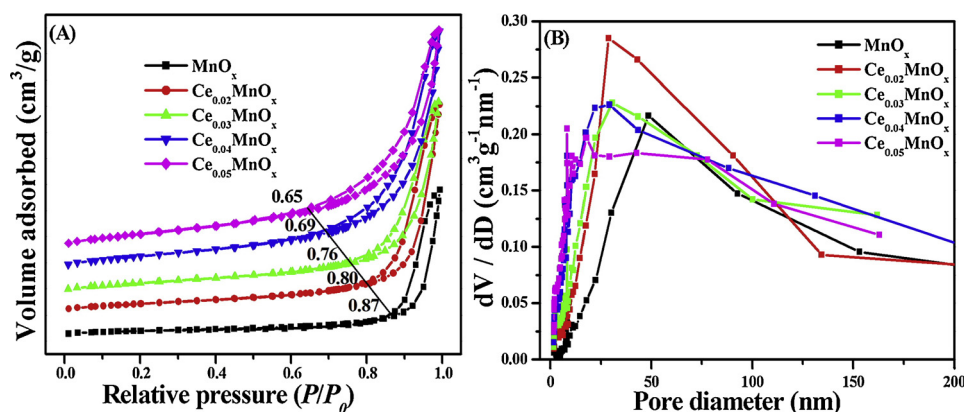


Fig. 2. N<sub>2</sub> adsorption-desorption isotherms (A) and the pore size distribution (B) of Ce<sub>0.05</sub>MnO<sub>x</sub>.

Ce, which hindered the further assembly of Ce<sub>0.05</sub>MnO<sub>x</sub> crystal, and result in the smaller crystal size and hollow shell structure with open mouth.

### 3.4. TEM images

The TEM images of MnO<sub>x</sub> (Fig. 4(a)–(c)), Ce<sub>0.02</sub>MnO<sub>x</sub> (Fig. 4(d)–(f)) and Ce<sub>0.03</sub>MnO<sub>x</sub> (Fig. 4(g)–(i)) are presented in Fig. 4. It can be seen that all samples are hierarchical structure assembled by particles. The average particle sizes of MnO<sub>x</sub>, Ce<sub>0.02</sub>MnO<sub>x</sub> and Ce<sub>0.03</sub>MnO<sub>x</sub> is about 21, 18 and 17 nm, respectively, which is agreement with the results of XRD (Table 1). In the HRTEM image of MnO<sub>x</sub> (Fig. 4c), the lattice fringes are clear and demonstrate the (211) and (222) planes corresponding to the phase bixbyite Mn<sub>2</sub>O<sub>3</sub>. The lattice stripes of Ce<sub>0.02</sub>MnO<sub>x</sub> are not obvious, but the lattice stripes of (211) and (222) still can be observed in Fig. 4(f). However, the lattice fringes of the Ce<sub>0.03</sub>MnO<sub>x</sub> (Fig. 4i) are unclear due to the much weaker crystallinity and it is consistent with the XRD results, confirming the decrease in the crystallinity of Ce<sub>0.03</sub>MnO<sub>x</sub>. In addition, defects can be clearly seen at the junction of particles in the HRTEM image of Ce<sub>0.05</sub>MnO<sub>x</sub>, suggesting that hierarchical structure can cause more defects derived from the Ce addition [45].

### 3.5. H<sub>2</sub>-TPR analysis

The oxidation and reduction behavior of the catalysts is analyzed by H<sub>2</sub>-TPR displayed in Fig. 5. For MnO<sub>x</sub>, three H<sub>2</sub> consumption peaks in the range of 163–238, 238–327 and 327–420 °C are detected. The peak in the range of 163–238 °C is ascribed to the reduction of surface adsorbed oxygen species. The peaks in the range of 238–327 and

327–420 °C belong to the reduction of MnO<sub>2</sub>/Mn<sub>2</sub>O<sub>3</sub> to Mn<sub>3</sub>O<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub> to MnO, respectively [46–48]. For Ce<sub>0.05</sub>MnO<sub>x</sub>, the three reduction peaks are still observed. The reduction peak in the range of 75–300 °C is magnified and shown in the left of Fig. 5. It is noticed that the initial reduction temperature decrease gradually, the peak broadens and the intensity increases gradually with the increase of the Ce content. This indicates that there is more abundance of surface adsorbed oxygen species on Ce<sub>0.05</sub>MnO<sub>x</sub>, which is also confirmed by the O<sub>2</sub>-TPD results displayed in Fig. S3. In addition, compared with MnO<sub>x</sub>, the second reduction peak belongs to the reduction of MnO<sub>2</sub>/Mn<sub>2</sub>O<sub>3</sub> to Mn<sub>3</sub>O<sub>4</sub> shifts slightly to the high temperature. Moreover, it can be seen that the third peak also shifts to high temperature with increasing the Ce content, but the peak shift to low temperature when the Ce content is more than 3%. The above results suggest the existence of the strong interaction between Ce and Mn oxides in Ce<sub>0.05</sub>MnO<sub>x</sub> [49], which is closely related to the outstanding redox capacity of MnO<sub>x</sub> [50] and strong store and release oxygen of Ce oxide [51].

### 3.6. XPS study

The XPS is used to analyze the surface information including the surface atomic concentration and chemical states of the elements. The results are depicted in Fig. 6.

The Mn2p spectra of MnO<sub>x</sub> and Ce<sub>0.05</sub>MnO<sub>x</sub> are fitted three main spin-orbital lines at 640.45, 641.65 and 642.9 eV (Fig. 6A), which are ascribed to the Mn<sup>2+</sup>, Mn<sup>3+</sup> and Mn<sup>4+</sup> species, respectively [15,52]. The percentage of these species is calculated by the area ratio, and the results are listed in Table 2. The percentage of Mn<sup>4+</sup> (Mn<sup>4+</sup> to (Mn<sup>4+</sup> +

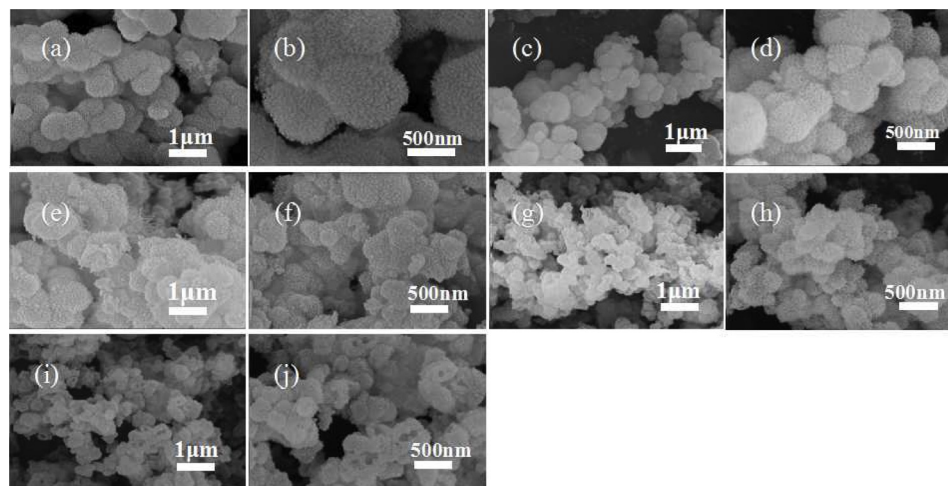


Fig. 3. SEM images of MnO<sub>x</sub> (a and b), Ce<sub>0.02</sub>MnO<sub>x</sub> (c and d), Ce<sub>0.03</sub>MnO<sub>x</sub> (e and f), Ce<sub>0.04</sub>MnO<sub>x</sub> (g and h), Ce<sub>0.05</sub>MnO<sub>x</sub> (i and j).



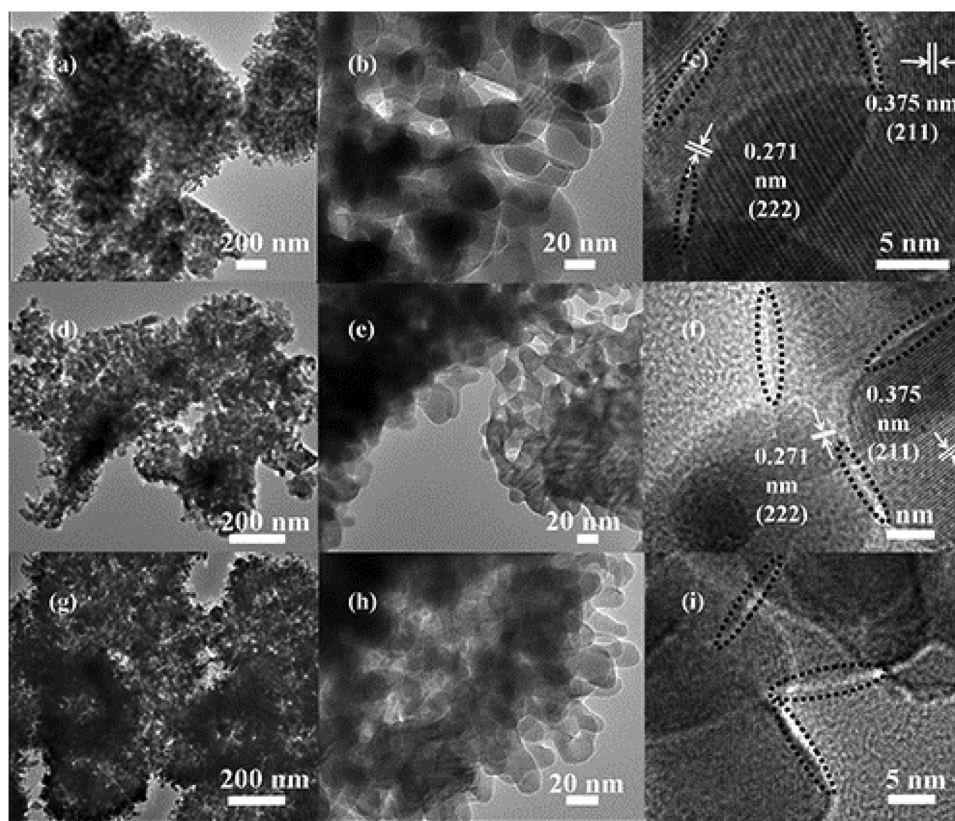


Fig. 4. TEM images of MnO<sub>x</sub> (a, b and c), Ce<sub>0.02</sub>MnO<sub>x</sub> (d, e and f) and Ce<sub>0.03</sub>MnO<sub>x</sub> (g, h and i).

Mn<sup>3+</sup> + Mn<sup>2+</sup>)) is 27.2%, 33.6%, 34.9%, 32.8% and 31.4% over MnO<sub>x</sub>, Ce<sub>0.02</sub>MnO<sub>x</sub>, Ce<sub>0.03</sub>MnO<sub>x</sub>, Ce<sub>0.04</sub>MnO<sub>x</sub> and Ce<sub>0.05</sub>MnO<sub>x</sub>, respectively. It is observed that the percentage of Mn<sup>4+</sup> on Ce<sub>a</sub>MnO<sub>x</sub> is more than that on MnO<sub>x</sub>, moreover, the change of the Mn<sup>4+</sup> content presents volcano type with the increase of the Ce content (Fig. S4(A)). It is worth mentioning that Ce<sub>0.03</sub>MnO<sub>x</sub> has the highest Mn<sup>4+</sup> content (34.9%) among the Ce<sub>a</sub>MnO<sub>x</sub> samples. The results indicate that the addition of Ce can improve the formation of the surface Mn<sup>4+</sup> species, and the incorporation of moderate Ce leads to the most amount of the surface Mn<sup>4+</sup> species.

For the Ce3d spectra (Fig. 6B), eight peaks can be fitted by deconvolution according to the literatures [53,54]. The peaks at 881.7, 887.5, 897.4, 900.2, 906.9 and 916.3 eV denoted as V, V', V'', U, U' and U''

are attributed to the Ce<sup>4+</sup> species, and the peaks at 883.3 and 903.5 eV are assigned to the Ce<sup>3+</sup> species which are denoted as V' and U'. The calculated results of the correlative Ce<sup>4+</sup> and Ce<sup>3+</sup> percentage based on the peaks area are listed in Table 2. It is noteworthy that the ratio of Ce<sup>3+</sup> to (Ce<sup>4+</sup> + Ce<sup>3+</sup>) (Ce<sup>3+</sup>/Ce) is 21.7%, 23.7%, 20.1% and 18.5% for Ce<sub>0.02</sub>MnO<sub>x</sub>, Ce<sub>0.03</sub>MnO<sub>x</sub>, Ce<sub>0.04</sub>MnO<sub>x</sub> and Ce<sub>0.05</sub>MnO<sub>x</sub>, respectively, which indicate that the proportion of Ce<sup>3+</sup>/Ce increases with the Ce content, and then decreases gradually. In other words, there is a volcano type relation between the surface Ce<sup>3+</sup>/Ce ratio and the Ce content in Ce<sub>a</sub>MnO<sub>x</sub> (Fig. S4(B)). Meanwhile, the surface Ce<sup>3+</sup> amount of the Ce<sub>0.03</sub>MnO<sub>x</sub> catalyst is higher than that of the others.

Interestingly, combined the XPS results of Mn and Ce, it is found that there is a linear relation between the surface Mn<sup>4+</sup>/Mn ratio and

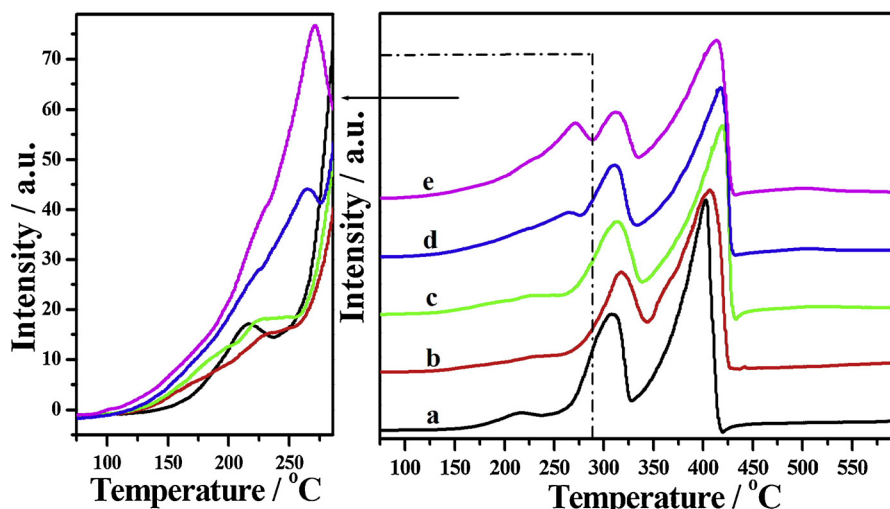


Fig. 5. H<sub>2</sub>-TPR profiles of MnO<sub>x</sub> (a), Ce<sub>0.02</sub>MnO<sub>x</sub> (b), Ce<sub>0.03</sub>MnO<sub>x</sub> (c), Ce<sub>0.04</sub>MnO<sub>x</sub> (d) and Ce<sub>0.05</sub>MnO<sub>x</sub> (e).

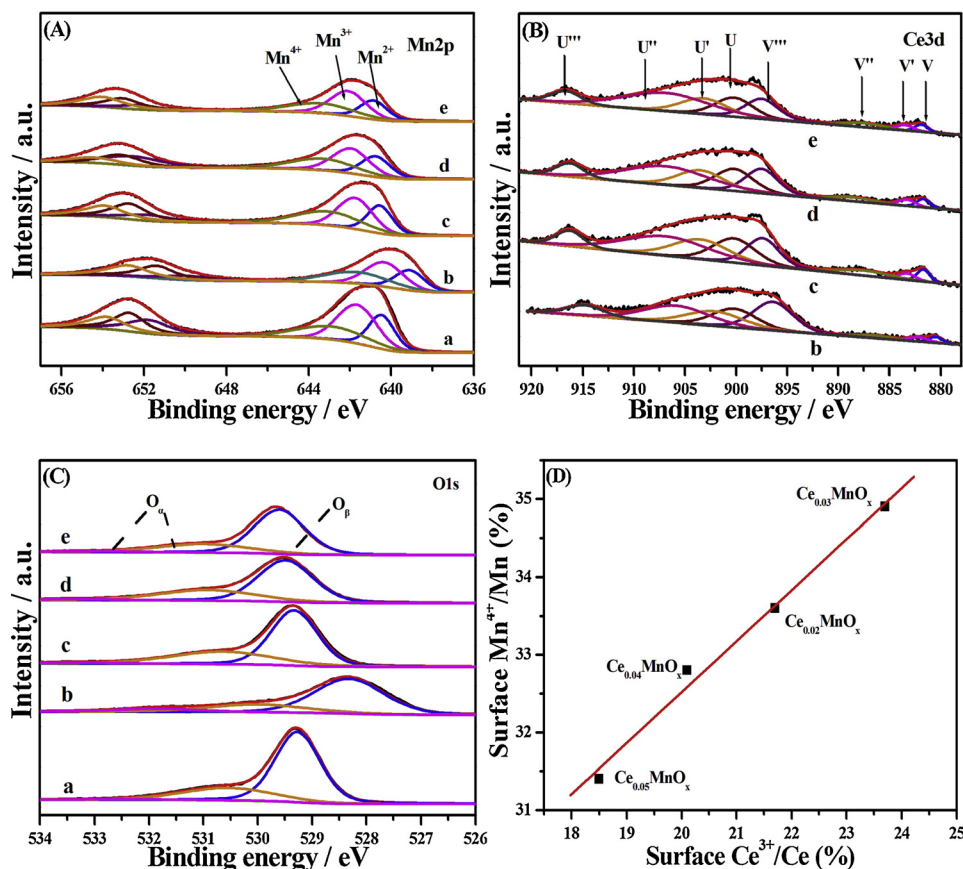


Fig. 6. XPS for (A) Mn2p, (B) Ce 3d, (C) O 1s of MnO<sub>x</sub> (a), Ce<sub>0.02</sub>MnO<sub>x</sub> (b), Ce<sub>0.03</sub>MnO<sub>x</sub> (c), Ce<sub>0.04</sub>MnO<sub>x</sub> (d) and Ce<sub>0.05</sub>MnO<sub>x</sub> (e), (D) relation between surface Mn<sup>4+</sup>/Mn and surface Ce<sup>3+</sup>/Ce of Ce<sub>a</sub>MnO<sub>x</sub>.

the surface Ce<sup>3+</sup>/Ce ratio (Fig. 6D). Thus, it is suggested that the addition of Ce in Ce<sub>a</sub>MnO<sub>x</sub> may be cause the oxidation reduction cycle like Mn<sup>3+</sup> + Ce<sup>4+</sup> ⇌ Mn<sup>4+</sup> + Ce<sup>3+</sup> [55,56], confirming the strong interaction between Ce and Mn. That is to say, it is favor of producing more amounts of the surface Mn<sup>4+</sup> and Ce<sup>3+</sup> species accompanied by moderate Ce content in the Ce<sub>0.03</sub>MnO<sub>x</sub> catalysts.

As displayed in Fig. 6C, the XPS of O 1s can be fitted into three peaks, the low binding energy peak at 528.5–529.8 eV is attributed to the lattice oxygen (O<sub>β</sub>). Two shoulder peaks at 531.9–533.1 and 530.1–531.3 eV are ascribed to the chemisorbed water and the surface adsorbed oxygen (O<sub>α</sub>) such as O<sub>2</sub><sup>2-</sup>, O<sub>2</sub>, a part of defect oxide or hydroxyl-like groups, respectively [16,43,54,57]. With the increase of Ce content, the O<sub>α</sub> content (O<sub>α</sub>/(O<sub>α</sub> + O<sub>β</sub>)) also increases gradually, which is compliance with the results of H<sub>2</sub>-TPR and O<sub>2</sub>-TPD. It may be because of strong interaction between Ce and Mn (Table 2).

From the above XPS results, a small amount of Ce doping can reduce the content of the surface Mn<sup>3+</sup>, and increase the content of surface

Mn<sup>4+</sup>, Ce<sup>3+</sup> and O<sub>α</sub> species. This indicates that Ce doping can result in the redox reaction between Ce<sup>4+</sup> and Mn<sup>3+</sup> to produce the more amounts of Mn<sup>4+</sup> species. The presence of Ce<sup>3+</sup> may lead to the charge imbalance than can form oxygen vacancies and unsaturated chemical bonds on the surface of catalyst. In other words, this situation will generate more additional chemisorbed oxygen or weakly adsorbed oxygen species on the surface of the Ce<sub>a</sub>MnO<sub>x</sub> catalysts and the chemisorbed oxygen is more reactive than the lattice oxygen due to its much higher mobility [55].

Another interesting finding is that the surface and bulk atomic concentration of Ce and Mn are different obviously based on the detected results of XRF and XPS. According to the XRF results, the atomic ratio of Ce to Mn (Ce/Mn) in bulk is 0.014, 0.019, 0.029 and 0.030 for Ce<sub>0.02</sub>MnO<sub>x</sub>, Ce<sub>0.03</sub>MnO<sub>x</sub>, Ce<sub>0.04</sub>MnO<sub>x</sub> and Ce<sub>0.05</sub>MnO<sub>x</sub>, respectively. Nevertheless, the corresponding Ce/Mn atomic ratios on surface of these samples are 0.15, 0.16, 0.18 and 0.19, which are much higher than those in the bulk Ce<sub>a</sub>MnO<sub>x</sub>. These results confirm that a large

Table 2

XPS data and activity results of the MnO<sub>x</sub> and Ce<sub>a</sub>MnO<sub>x</sub> catalysts.

Catalysts	O (%)	Mn (%)	Ce (%)	Ce/Mn <sup>a</sup>	Mn <sup>4+</sup> /Mn <sup>b</sup> (%)	O <sub>α</sub> /O <sup>c</sup> (%)	Ce <sup>3+</sup> /Ce <sup>d</sup> (%)	T <sub>50</sub> (°C)	T <sub>100</sub> (°C)	Ea (kJ/mol)
MnO <sub>x</sub>	58.3	41.7	–	–	27.2	29	–	241	251	155.2
Ce <sub>0.02</sub> MnO <sub>x</sub>	58.9	35.8	5.3	0.148	33.6	33.9	21.7	221	230	98.0
Ce <sub>0.03</sub> MnO <sub>x</sub>	57.8	36.5	5.7	0.156	34.9	34.9	23.7	215	225	90.4
Ce <sub>0.04</sub> MnO <sub>x</sub>	56.2	37.2	6.6	0.177	32.8	36.2	20.1	225	235	91.5
Ce <sub>0.05</sub> MnO <sub>x</sub>	56.3	36.6	7.1	0.194	31.4	40.0	18.5	227	235	104.3

<sup>a</sup> The element content is measured by the XPS analysis.

<sup>b</sup> The ratio of surface Mn<sup>4+</sup> to (Mn<sup>4+</sup> + Mn<sup>3+</sup> + Mn<sup>2+</sup>).

<sup>c</sup> The ratio of surface Ce<sup>3+</sup> to (Ce<sup>4+</sup> + Ce<sup>3+</sup>).

<sup>d</sup> The ratio of surface O<sub>α</sub> to (O<sub>α</sub> + O<sub>β</sub>).

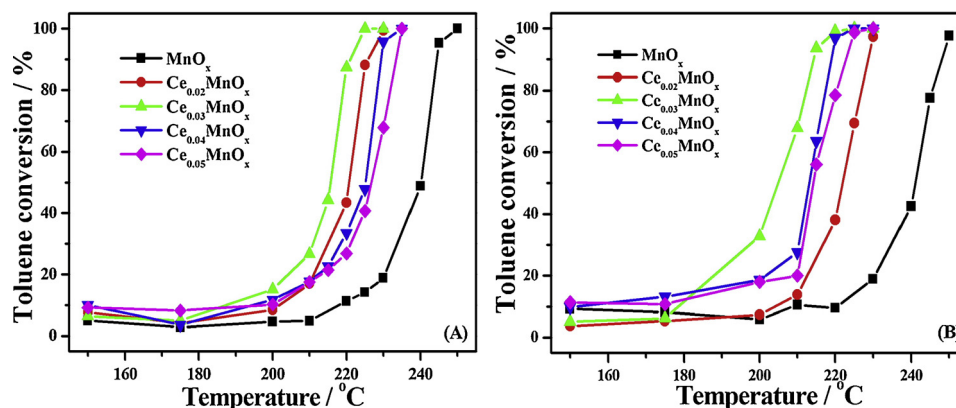


Fig. 7. Catalytic performance of toluene oxidation over the  $\text{MnO}_x$  and  $\text{Ce}_a\text{MnO}_x$  catalysts, (A) without  $\text{H}_2\text{O}$  and (B) with  $\text{H}_2\text{O}$ . [Reaction conditions:  $[\text{C}_7\text{H}_8] = 1000 \text{ ppm}$ ,  $[\text{O}_2] = 20\%$ , and  $\text{N}_2$  balance].

proportion of Ce should be dispersed on the surface of the  $\text{Ce}_a\text{MnO}_x$  samples. Ce oxide package on the surface of the  $\text{Ce}_a\text{MnO}_x$  particle after adding Ce to  $\text{MnO}_x$ . There is a strong interaction between Ce and Mn by an oxidation reduction cycle of  $\text{Mn}^{3+} + \text{Ce}^{4+} \leftrightarrow \text{Mn}^{4+} + \text{Ce}^{3+}$ . And the interaction not only causes the crystal size decrease gradually, but also hinders to the further growth of  $\text{Ce}_a\text{MnO}_x$ . In other word, the strong interaction between Ce and Mn leads to the morphology change of  $\text{Ce}_a\text{MnO}_x$ . The influences of the strong interaction between Mn and Ce on the formation of the hollow shells with open mouths in  $\text{Ce}_{0.04}\text{MnO}_x$  and  $\text{Ce}_{0.05}\text{MnO}_x$ . Ce need to be investigated systematically by a lot of experiments in our future work.

### 3.7. Catalytic activity

The catalytic activities of the  $\text{Ce}_a\text{MnO}_x$  samples are investigated by using catalytic toluene combustion as model reaction.  $\text{CO}$ , benzaldehyde and benzoic acid etc. were not detected except  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in our experiment condition [38,47,58]. Fig. 7(A) displays the conversion of toluene as function of the reaction temperature. For the  $\text{MnO}_x$  catalyst, it is observed that the toluene conversion is less than 5% below  $210^\circ\text{C}$ . And then the toluene conversion gradually rises with the increase of reaction temperature, and increases rapidly when the reaction temperature is above  $230^\circ\text{C}$ . Especially, the temperature at the toluene conversion of 50% ( $T_{50}$ ) and 100% ( $T_{100}$ ) is 240 and  $250^\circ\text{C}$ , respectively. For  $\text{Ce}_a\text{MnO}_x$ ,  $T_{50}$  is 221, 215, 225 and  $227^\circ\text{C}$  over the  $\text{Ce}_{0.02}\text{MnO}_x$ ,  $\text{Ce}_{0.03}\text{MnO}_x$ ,  $\text{Ce}_{0.04}\text{MnO}_x$  and  $\text{Ce}_{0.05}\text{MnO}_x$  catalysts, respectively, corresponding the  $T_{100}$  is 230, 225, 235 and  $235^\circ\text{C}$ . Obviously, catalytic performance of  $\text{Ce}_a\text{MnO}_x$  is higher than that of  $\text{MnO}_x$ . The results suggest that addition of Ce could increase combustion efficiency of toluene compared with  $\text{MnO}_x$ . Meanwhile, it is quite clear that the  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst exhibits the best catalytic performance for toluene combustion. Besides, the  $T_{50}$  and  $T_{100}$  for  $\text{Ce}_{0.03}\text{MnO}_x$  are  $25^\circ\text{C}$  lower than those of  $\text{MnO}_x$ . The above results indicate that there is also a striking improvement of catalytic toluene combustion while adding a small amount of Ce to  $\text{MnO}_x$ , however, doping more Ce can lead to the decrease of the activity. Thus, the  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst shows superior catalytic property for the toluene combustion, which is associated with the proper Ce content. Moreover, the  $\text{O}_2$ -TPSR results also confirm that only  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and no other products are detected over  $\text{Ce}_{0.03}\text{MnO}_x$  in Fig. S5, indicating that  $\text{Ce}_{0.03}\text{MnO}_x$  shows outstanding deep oxidation activity, which is consistent with the result of literatures [38,47,59].

In order to investigate the effect of  $\text{H}_2\text{O}$  on the catalytic activity, 5% of  $\text{H}_2\text{O}$  is introduced into the feed during the test, and the results are displayed in the Fig. 7(B). As shown in Figure,  $T_{50}$  is 240, 220, 205, 213,  $214^\circ\text{C}$  over  $\text{MnO}_x$ ,  $\text{Ce}_{0.02}\text{MnO}_x$ ,  $\text{Ce}_{0.03}\text{MnO}_x$ ,  $\text{Ce}_{0.04}\text{MnO}_x$  and  $\text{Ce}_{0.05}\text{MnO}_x$  catalysts, respectively, and corresponding  $T_{100}$  is 250, 235,

220, 225,  $230^\circ\text{C}$ . It is found that the toluene conversion with  $\text{H}_2\text{O}$  slightly decrease compared with that without  $\text{H}_2\text{O}$  over  $\text{MnO}_x$  and  $\text{Ce}_{0.02}\text{MnO}_x$ . However, it is noteworthy that the toluene conversion with  $\text{H}_2\text{O}$  is much higher than that without  $\text{H}_2\text{O}$  for the  $\text{Ce}_{0.03}\text{MnO}_x$ ,  $\text{Ce}_{0.04}\text{MnO}_x$  and  $\text{Ce}_{0.05}\text{MnO}_x$  catalysts at the same reaction temperature. It can be concluded that the catalytic activities are improved after the addition of 5 vol.%  $\text{H}_2\text{O}$  over the  $\text{Ce}_{0.03}\text{MnO}_x$ ,  $\text{Ce}_{0.04}\text{MnO}_x$  and  $\text{Ce}_{0.05}\text{MnO}_x$  catalysts.

The dynamics parameters are calculated under the conversion of less than 30% (Fig. S6). As shown in the Table 2, the apparent activation energy ( $E_a$ ) obtained from Arrhenius plots is 155.2, 98.0, 90.4, 91.5 and  $104.3 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{MnO}_x$ ,  $\text{Ce}_{0.02}\text{MnO}_x$ ,  $\text{Ce}_{0.03}\text{MnO}_x$ ,  $\text{Ce}_{0.04}\text{MnO}_x$  and  $\text{Ce}_{0.05}\text{MnO}_x$ , respectively. The  $E_a$  values over  $\text{Ce}_a\text{MnO}_x$  are much lower than that over  $\text{MnO}_x$ , meanwhile, the  $E_a$  value of  $\text{Ce}_{0.03}\text{MnO}_x$  is the lowest among these  $\text{Ce}_a\text{MnO}_x$  catalysts, which is in good consistent with the results of catalytic activity.

Turnover number (TON), a fundamental measurement for catalytic reaction, refers to reaction cycles occurring on each active site over a period of time (1 min). The TON values on the basis of surface Mn content are calculated over the  $\text{Ce}_a\text{MnO}_x$  samples under both without  $\text{H}_2\text{O}$  and with  $\text{H}_2\text{O}$  at 200 and  $220^\circ\text{C}$ . The results are displayed in Fig. 8.  $\text{Ce}_{0.03}\text{MnO}_x$  exhibits the highest TON value at both 200 and  $220^\circ\text{C}$  under the feed without  $\text{H}_2\text{O}$  among these  $\text{Ce}_a\text{MnO}_x$  catalysts. It is noteworthy that the TON value changes a lot when  $\text{H}_2\text{O}$  is added to the reaction feed. In general, the TON values decrease slightly for the  $\text{MnO}_x$  and  $\text{Ce}_{0.02}\text{MnO}_x$  catalysts compare with those without  $\text{H}_2\text{O}$ . But the TON values are enhanced significantly with  $\text{H}_2\text{O}$  for the  $\text{Ce}_{0.03}\text{MnO}_x$ ,  $\text{Ce}_{0.04}\text{MnO}_x$  and  $\text{Ce}_{0.05}\text{MnO}_x$  catalysts. The TONs follow as the order:  $\text{Ce}_{0.03}\text{MnO}_x > \text{Ce}_{0.04}\text{MnO}_x > \text{Ce}_{0.05}\text{MnO}_x > \text{Ce}_{0.02}\text{MnO}_x > \text{MnO}_x$ , which coincide with the catalytic activity. The results show that the addition of Ce can improve the catalytic performance of the catalyst under the condition of  $\text{H}_2\text{O}$  supply. To sum up, the  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst possesses the highest TON value whether low or high conversion of toluene, so the  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst displays the best catalytic ability for toluene combustion.

### 3.8. Stability test and effect of WHSV

Normally, the industrial VOCs emission contains water, so the stability test with  $\text{H}_2\text{O}$  must be considered. The test is evaluated over the  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst under condition of  $20,000 \text{ mL}\cdot\text{g}^{-1} \cdot \text{h}^{-1}$  at  $240^\circ\text{C}$ . It can be seen from Fig. S7 that 100% toluene conversion is almost unchanged for 5 h when 5 vol.%  $\text{H}_2\text{O}$  is added in the feed. Moreover, the effect of 10 vol.%  $\text{H}_2\text{O}$  on toluene conversion is also negligible. When water content is increased to 20 vol.%, the toluene conversion decreases to about 96%. However, the conversion could restore to about 99% after removing the water vapor from the feed. From these results, it can



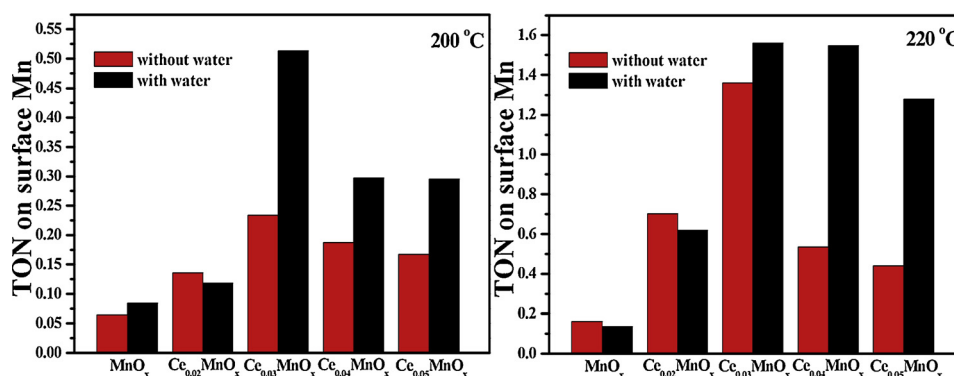


Fig. 8. TONs based on the surface Mn species over the Ce<sub>0.03</sub>MnO<sub>x</sub> catalysts at 200 and 220 °C.

be concluded that the Ce<sub>0.03</sub>MnO<sub>x</sub> catalyst still displays a great performance even under a mass of water vapor.

The stability test without H<sub>2</sub>O is also performed under condition of 20,000 mL·g<sup>-1</sup> h<sup>-1</sup> at 240 °C over Ce<sub>0.03</sub>MnO<sub>x</sub> due to its especial activity. As displayed in the Fig. S8(A), the toluene conversion remains unchanged (100%) for 60 h. Meanwhile, the toluene oxidation for three successive runs over Ce<sub>0.03</sub>MnO<sub>x</sub> is displayed in Fig. S8(B). It can be seen that T<sub>50</sub> is 215, 219 and 221 °C over the Ce<sub>0.03</sub>MnO<sub>x</sub> catalyst for 1 st, 2nd and 3rd run, respectively, corresponding the T<sub>100</sub> is 225, 225 and 226 °C, suggesting there is no obvious difference among the three successive runs. To sum up, the Ce<sub>0.03</sub>MnO<sub>x</sub> catalyst has good activity stability and it is crucial for practical application.

The effect of WHSV on toluene oxidation is also regarded as a key parameter. The toluene conversion over the Ce<sub>0.03</sub>MnO<sub>x</sub> catalyst under different WHSV of 20,000, 40,000 and 80,000 mL·g<sup>-1</sup> h<sup>-1</sup> is demonstrated in Fig. S9. When the WHSV is 40,000 mL·g<sup>-1</sup> h<sup>-1</sup>, the T<sub>50</sub> and T<sub>100</sub> are 228 and 240 °C, respectively, which are only 12 and 15 °C higher than those under 20,000 mL·g<sup>-1</sup> h<sup>-1</sup>. Similarly, when the WHSV increases to 80,000 mL·g<sup>-1</sup> h<sup>-1</sup>, the T<sub>50</sub> and T<sub>100</sub> increase 19 and 29 °C compared with the corresponding results at 20,000 mL·g<sup>-1</sup> h<sup>-1</sup>. Thus, the results indicate that the Ce<sub>0.03</sub>MnO<sub>x</sub> catalyst exhibits much better catalytic toluene combustion performance even under much higher WHSV.

### 3.9. In situ DRIFTS study

In order to study the surface adsorbed species and understand the catalytic reaction process of toluene combustion, the *in situ* DRIFTS experiments were performed over the MnO<sub>x</sub> and Ce<sub>0.03</sub>MnO<sub>x</sub> catalysts.

Fig. 9 displays the DRIFTS of MnO<sub>x</sub>(A) and Ce<sub>0.03</sub>MnO<sub>x</sub>(B) after being exposed to toluene + N<sub>2</sub> at 220 °C with different time interval. It can be seen that there is no characteristic peak at first 5 min on MnO<sub>x</sub> (Fig. 10(A)). And after 5 min, five absorption peaks are detected, and the peaks intensities gradually increase with extended time and unchanged till 50 min. The peak at 1329 cm<sup>-1</sup> is attributed to the skeletal C–C stretching vibration for benzaldehyde, and the bands at 1650 and 1693 cm<sup>-1</sup> are ascribed to the C=O stretching vibration of aldehydic. Furthermore, the peaks at 1404 and 1525 cm<sup>-1</sup> belong to the symmetric C–O stretching vibration and antisymmetric C–O stretching vibration of benzoate, respectively [60]. For Ce<sub>0.03</sub>MnO<sub>x</sub> (Fig. 9(B)), the peaks are observed obviously after 2 min, and the peaks intensity increases significantly reaching saturation after about 20 min. The bands at 1404, 1445 and 1534 cm<sup>-1</sup> are ascribed to symmetric C–O stretching vibration of benzoate, skeletal C–C stretching vibration of benzoate and antisymmetric C–O stretching vibration of benzoate, respectively. And the bands at 1551 and 1592 cm<sup>-1</sup> are attributed to skeletal C–C stretching vibration of the aromatic ring. The band at 3069 cm<sup>-1</sup> is assigned to phenylic C–H stretching vibration of aromatic ring [60–62]. It is noteworthy that the peaks belong to the benzaldehyde are not observed. Interestingly, the benzaldehyde and benzoic acid species are

formed on the MnO<sub>x</sub> catalyst after absorbing toluene, while only benzoic acid is detected on the surface of the Ce<sub>0.03</sub>MnO<sub>x</sub> catalyst. These results indicate toluene can be rapidly adsorbed and activated to the adsorbed benzoic acid species than the benzaldehyde species on the Ce<sub>0.03</sub>MnO<sub>x</sub> catalyst, suggesting the strong oxidation ability of the Ce<sub>0.03</sub>MnO<sub>x</sub> catalyst.

After the adsorption of toluene, 20% O<sub>2</sub> + N<sub>2</sub> is added into the IR cell at 220 °C. For MnO<sub>x</sub> (Fig. 9(C)), it's worth noting that the peaks at 1650 and 1693 cm<sup>-1</sup> assign to benzaldehyde clearly decrease and the peak at 1525 cm<sup>-1</sup> assign to benzoate slightly decrease after 40 min, which is attributed to the partial oxidation of the benzaldehyde species to benzoate in the process. It can be concluded that toluene could be absorbed on the MnO<sub>x</sub> catalyst and oxidated to aldehydic, then to benzaldehyde. For Ce<sub>0.03</sub>MnO<sub>x</sub> (Fig. 9(D)), the peaks intensities clearly decrease at 10 min and only much weaker bands can be observed after 30 min. On the basis of these results, it can be concluded that the toluene could be oxidized to benzoate and to CO<sub>2</sub> subsequently [63]. The above results demonstrate toluene can be oxidized more quickly over Ce<sub>0.03</sub>MnO<sub>x</sub> than over MnO<sub>x</sub>, which may be the main factor of excellent performance over the Ce<sub>0.03</sub>MnO<sub>x</sub> catalyst.

Furthermore, in order to understand the effect of H<sub>2</sub>O on the toluene oxidation, *in situ* DRIFTS tests of the toluene adsorption and reaction at 210 °C are carried out over Ce<sub>0.03</sub>MnO<sub>x</sub> based on the lower toluene conversion in activity evaluation under the condition with H<sub>2</sub>O and without H<sub>2</sub>O. The results are given in Fig. 10. The characteristic peaks of the toluene adsorption 210 °C are the same as those at 220 °C (Fig. 10(A)). It is noticed that the characteristic peaks almost disappear completely after introducing O<sub>2</sub>/N<sub>2</sub> without H<sub>2</sub>O for 80 min. However, when the O<sub>2</sub>/N<sub>2</sub> with H<sub>2</sub>O is introduced to the IR cell, the characteristic peaks nearly disappear after 40 min (Fig. 10(B)). Combined the above results, the introduction of water is beneficial to the catalytic reaction of toluene oxidation, which is consistent with the result of toluene conversion.

In addition, the experiments of temperature programmed desorption of toluene (Toluene TPD) also confirm above results. Toluene TPD is performed over the Ce<sub>0.03</sub>MnO<sub>x</sub> catalyst with different adsorption conditions. As shown in Fig. S10, only CO<sub>2</sub> desorption peak is detected without CO and toluene etc. For the toluene adsorption, the CO<sub>2</sub> desorption peak is observed at about 307 °C. When the toluene and O<sub>2</sub> are co-adsorbed on the Ce<sub>0.03</sub>MnO<sub>x</sub> catalyst, the CO<sub>2</sub> desorption peak is no significant difference with the result of pure toluene, but the peak intensities increase a lot, meaning O<sub>2</sub> could promote the adsorption of toluene. Furthermore, when the O<sub>2</sub>, H<sub>2</sub>O and toluene are co-adsorbed on Ce<sub>0.03</sub>MnO<sub>x</sub>, the temperature of the CO<sub>2</sub> desorption peak decreases obviously (about 274 °C), the results suggest the co-adsorption of O<sub>2</sub>/H<sub>2</sub>O promote the reaction of toluene. In other words, the addition of water can promote the adsorption and activation of toluene. Thus, according to the literatures [63,64], we think the introduction of water promotes the adsorption and activation of toluene and oxygen leading to the much better activity of toluene combustion over the



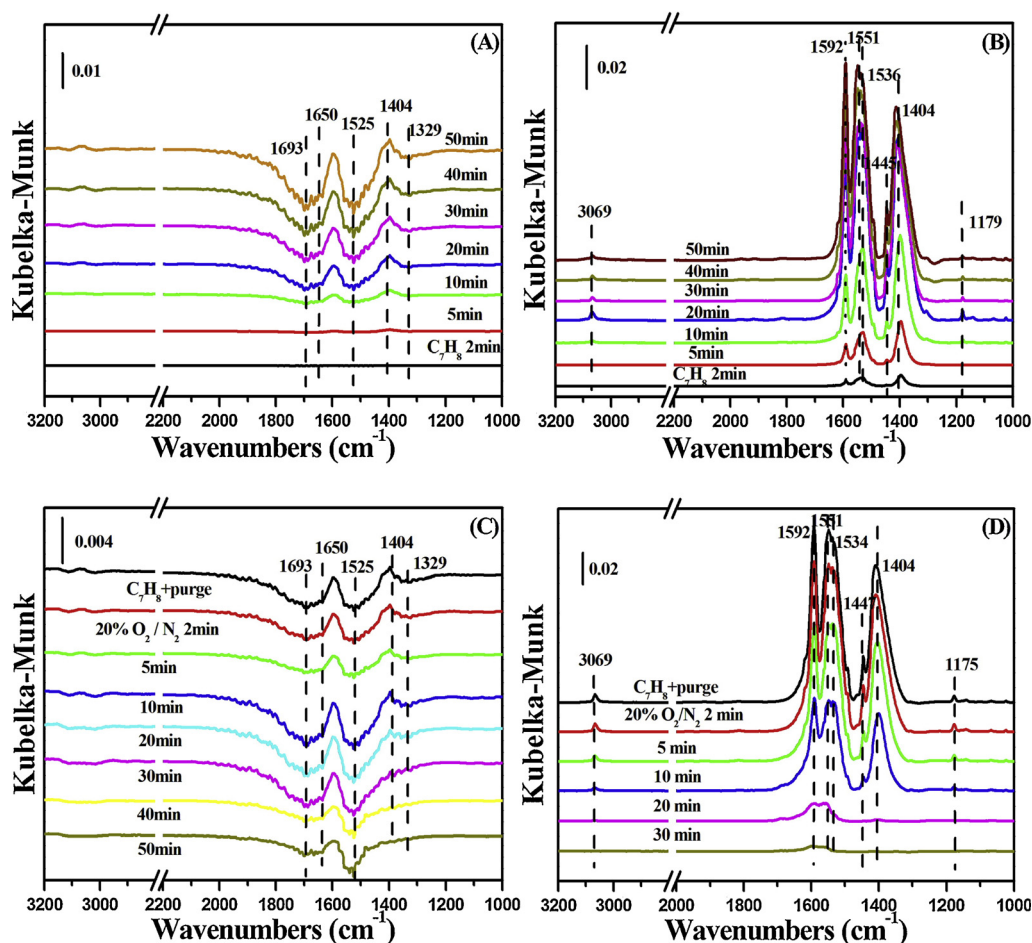


Fig. 9. *In situ* DRIFTS of toluene adsorption for different time over  $\text{MnO}_x$  (A) and  $\text{Ce}_{0.03}\text{MnO}_x$  (B); after inputting  $20\% \text{O}_2/\text{N}_2$  over  $\text{MnO}_x$  (C) and  $\text{Ce}_{0.03}\text{MnO}_x$  (D) at 220 °C.

$\text{Ce}_{0.03}\text{MnO}_x$  catalyst. It is reported that the introduction of  $\text{H}_2\text{O}$  can lead to the appearance of hydroperoxyl-like, which is benefit of the activation O–O bond, enhancing the catalyst activity of toluene oxidation [64,65]. A detailed study on the role of  $\text{H}_2\text{O}$  needs to be carried out in the future.

### 3.10. Effect of Ce

To sum up, doping of Ce could efficiently promote the toluene

combustion activity of the  $\text{Ce}_a\text{MnO}_x$  catalysts, meanwhile, the  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst reveals the best activity among these catalysts. According to the results of various characterizations, it can be concluded that there is strong interaction between Ce and Mn, which improve the formation of more surface adsorbed oxygen and surface  $\text{Mn}^{4+}$  species that are favor of the adsorption and activation of toluene.

Compared the Ce/Mn atomic ratio in bulk with on surface, it is obvious that the Ce/Mn ratio on the surface of  $\text{Ce}_a\text{MnO}_x$  is much higher than that in bulk of the catalysts. It indicates the Ce mainly disperses on

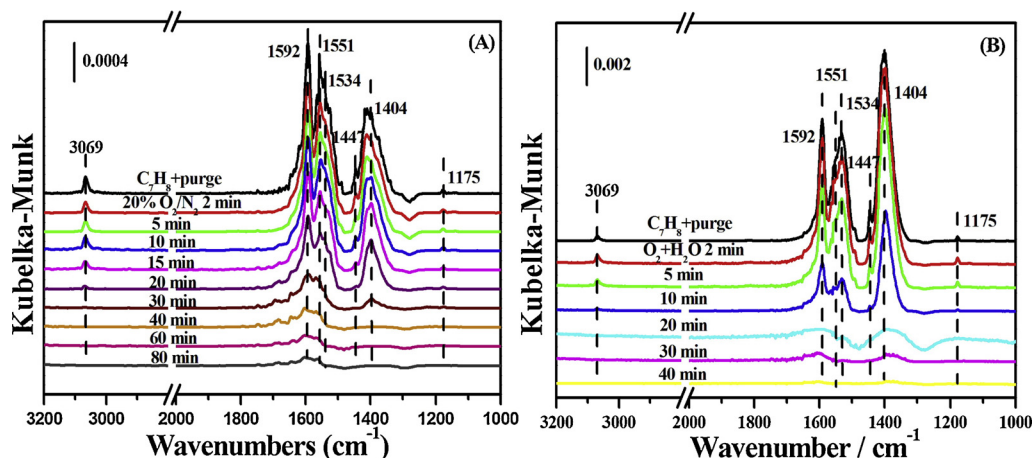


Fig. 10. *In situ* DRIFTS under  $20\% \text{O}_2/\text{N}_2$  (A) and  $20\% \text{O}_2/\text{N}_2$  with  $\text{H}_2\text{O}$  over  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst before pre-adsorbed toluene at 210 °C.

the surface of  $\text{Ce}_x\text{MnO}_x$ , which result in the smaller particle sizes verified by XRD and TEM. Moreover, the strong interaction between Ce and Mn hinders the further increase of the  $\text{Ce}_x\text{MnO}_x$  particles to form the microsphere structure smaller hollow shell structure with open mouth, leading to much higher BET surface area. This is due to the strong interaction between Mn and Ce which is confirmed by XRD and Raman. Besides, there are more defects formed after doping Ce element verified by TEM. XPS results also prove that the introduction of the Ce not only lead to produce more of the chemical adsorption oxygen species on the catalyst, but also can form more surface  $\text{Mn}^{4+}$  species by the reaction ( $\text{Mn}^{3+} + \text{Ce}^{4+} \leftrightarrow \text{Mn}^{4+} + \text{Ce}^{3+}$ ) [55,56], which contribute to the activity of toluene oxidation. However, when too much Ce is added for  $\text{Ce}_{0.05}\text{MnO}_x$ , Ce oxide covers the surface of  $\text{Ce}_x\text{MnO}_x$ , thus reducing the active sites on the surface of the catalyst and weakening the activity. So the  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst exhibits the best catalytic activity, much better thermal stability and water resistance among the  $\text{Ce}_x\text{MnO}_x$  catalysts even under the WHSV of  $80,000 \text{ mL} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ .

Furthermore, the *in situ* DRIFTS prove that the adsorption speed and amount of toluene are much faster and more on the  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst than those on the  $\text{MnO}_x$  catalyst. Especially, toluene could be activated directly to form benzoic acid over  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst than benzaldehyde and benzoic on  $\text{MnO}_x$ . Moreover, the benzoic acid species over  $\text{Ce}_{0.03}\text{MnO}_x$  catalyst can be oxidized quickly to  $\text{CO}_2$ . Therefore, Ce addition can enhance the oxidation ability and improve adsorption and activation of toluene for  $\text{Ce}_{0.03}\text{MnO}_x$ .

#### 4. Conclusion

In this work, a series of hollow hierarchical structure  $\text{Ce}_x\text{MnO}_x$  materials like arbutus are prepared by redox co-precipitation method for catalytic toluene combustion. The various characterization results verify the strong interaction between Ce and Mn lead to the changes in the morphology of catalysts and form more defects with the Ce addition. Therefore, there are more surface adsorption oxygen and the surface  $\text{Mn}^{4+}$  species on  $\text{Ce}_x\text{MnO}_x$  compared with  $\text{MnO}_x$ . Among these  $\text{Ce}_x\text{MnO}_x$  catalysts,  $\text{Ce}_{0.03}\text{MnO}_x$  exhibits the optimum catalytic performance that the  $T_{50}$  and  $T_{100}$  are  $25^\circ\text{C}$  lower than those of  $\text{MnO}_x$  as well as much higher stability and  $\text{H}_2\text{O}$  resistance due to the abundant surface oxygen and  $\text{Mn}^{4+}$  species. Especially, the introduction of  $\text{H}_2\text{O}$  in the feed enhances the catalytic activity over  $\text{Ce}_{0.03}\text{MnO}_x$ , which may be related to the improvement of toluene adsorption and oxygen activation by  $\text{H}_2\text{O}$ . Furthermore, the reaction process investigation indicates that toluene can be rapidly adsorbed and activated to form the benzoic acid species without benzaldehyde on the surface of  $\text{Ce}_{0.03}\text{MnO}_x$ , and then is oxidized quickly to  $\text{CO}_2$  compared with  $\text{MnO}_x$ . This also explains why  $\text{Ce}_{0.03}\text{MnO}_x$  has better catalytic activity.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.01.005>.

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